

where n is the principal quantum number of the outermost s electron in the core. Now $\phi_{\nu s}(r) \rightarrow \text{const}$ and $V(r) \rightarrow -\infty$ as $r \rightarrow 0$, so that $V+V_R$ contains an uncancelled spike $-Ze^2/r$ of radius r_K . Now r_K is approximately a_0/Z , where a_0 is the Bohr radius, so that in first-order perturbation on ϕ the spike contributes an energy of about $4\pi|\phi(0)|^2 Z r_K^2 \sim 1/Z$ rydbergs which is unimportant for large Z .

Table I also shows how the radii r_a of the alkali atoms increase significantly with Z . Part of this is due to the decreasing ϵ_s since $\phi_{1s} \sim \exp[-(\epsilon_s)^{1/2}r]$ at large r , giving $r_a \propto \epsilon_s^{-1/2}$. However, the observed increase in r_a is considerably greater than this, and must be due to the fact that good cancellation inside the core pushes ϕ out to the regions of negative potential energy outside the core.

We turn now to the other monovalent series, the noble metals. Their ϵ_s ionization energies are rather larger than those of the alkalis:

$$\text{Ag, 7.57 eV; Cu, 7.72 eV; Au, 9.22 eV.} \quad (32)$$

The reason for this is as follows. In copper, for example, the $3d$ shell is rather loosely bound compared with the cores of the alkali atoms, and consequently extends out to a considerably larger radius than the $3s$ function. Thus the $3s$ function in (31) is incapable of cancelling off the potential in the outer regions of the core, leaving

a large negative potential which produces a tightly bound $4s$ level, i.e., a large ϵ_s . Thus the looser the d shell, the tighter the next s shell is; and if we take the order of increasing looseness of the d shells as Ag, Cu, Au as evidenced by their color and chemical valencies, we note that this is indeed the same as their order of increasing ϵ_s in (32).

A rough theory has already been given in reference 1 relating the electronic band structures of the alkali metals to the atomic parameters $\epsilon_s - \epsilon_p$ and r_a , and the argument seems to be applicable qualitatively also to groups IIA and IIIA of the periodic table. In Na, Mg, Al, the band gaps appear to be very small.³¹ As Z increases, ϵ_s ($\propto r_a^{-2}$) decreases more rapidly than $\epsilon_s - \epsilon_p$, resulting in an increasing band gap with the s -like state at the gap being the lower one. In Li and Be, however, there are large band gaps with the p -like state lowest, due to the small r_a and the abnormally low $\epsilon_s - \epsilon_p$ which we have seen is in turn due to the absence of a $1p$ shell. As Ziman³¹ has pointed out, these systematic trends in the band structures are directly reflected in the electrical resistivities and Hall coefficients³² of these metals as well as in other properties.

³¹ F. Ham, J. M. Ziman, and other contributors, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960).

³² J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960), p. 488.

Configuration Interaction in Simple Atomic Systems*†

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The ground-state wave functions of the helium, lithium, and beryllium atoms were approximated by a superposition of configurations with expansion lengths ranging from 35 for helium to 55 for beryllium. The discrepancies in the total energy are 0.014 eV for helium, 0.026 eV for lithium, and 0.17 eV for beryllium. A 19-configuration function was also applied to the lowest 3S state of helium, with a resulting accuracy of 0.0005 eV. The calculations were also made on all the isoelectronic series of ions through $Z=8$, the discrepancy remaining of the same order of magnitude but increasing with increasing Z . A lower bound to the electron affinity of lithium is set at 0.4773 eV, with the most probable value, obtained by extrapolating the isoelectronic series, being placed at 0.62 eV.

INTRODUCTION

PROBABLY the most widely used and most generally successful approach to many-particle quantum mechanics is the independent-particle model, which at its best is represented by the Hartree-Fock approxima-

tion.¹ Physically, this approximation amounts to treating the interparticle interactions in only an average fashion, i.e., each particle is assumed to move in only the average field of all the other particles of the system. Mathematically, the method consists of approximating the state function as an antisymmetrized product of one-particle functions (spin orbitals). Subjecting such a function to the variational principle leads to the well-

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¹ D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

known self-consistent-field (SCF) equations for the one-particle functions.

While this model is extremely useful for many purposes, it has a fundamental shortcoming. Since the wave equation is not separable in the individual particle coordinates, the many-electron eigenfunction can never be written as an antisymmetrized orbital product. Physically, this means that the details of the way in which the particles mutually correlate their motions is not adequately represented. There are two general methods of surpassing the basic approximations of the independent-particle model: (1) Explicitly introduce the interparticle coordinates r_{ij} into the trial wave function. (2) Write the trial wave function as a linear combination of antisymmetrized products of one-electron functions (commonly called configuration interaction). The first procedure has met with great success for two-electron systems such as helium-like atoms and the hydrogen molecule.^{2,3} It has established the energy eigenvalues for the helium isoelectronic series within the current limits of experimental error.⁴ However, it suffers from the extreme computational difficulty involved in extending it to larger systems. One attempt has been made to do the exactly analogous type of calculation for the lithium atom,⁵ which gave good results, although nowhere near the accuracy obtained for helium. The second method (configuration interaction), while it can be readily applied to any system within reach of *ab initio* calculations, has always been plagued with the difficulty of slow convergence.

The primary purpose of the present research is to make a thorough investigation of the method of configuration interaction to see just how well one can expect to do with expansion lengths which are still tractable on present-day computing equipment. The systems chosen were the lowest 1S and 3S states of the helium atom, the lowest 2S state of lithium, and the lowest 1S state of beryllium, and the respective isoelectronic series through $Z=8$. The list thus includes an excited triplet and several systems with more than a single closed shell.

A second purpose, of course, is to produce wave functions which should be a reasonable compromise between accuracy of approximation and usability, and hence useful for studying properties like diamagnetic susceptibilities, hyperfine splitting, transition probabilities, etc. A third purpose grew up in the course of the investigation, namely an attempt to predict the stability of the isoelectronic negative ions.

² E. Hylleraas and J. Mittdal, *Phys. Rev.* **103**, 829 (1956); T. Kinoshita, *ibid.* **115**, 366 (1959); W. Kolos, C. C. J. Roothaan, and R. Sack, *Revs. Modern Phys.* **32**, 178 (1960).

³ H. M. James and A. S. Coolidge, *J. Chem. Phys.* **1**, 825 (1933); W. Kolos and C. C. J. Roothaan, *Revs. Modern Phys.* **32**, 219 (1960).

⁴ C. L. Pekeris, *Phys. Rev.* **112**, 1649 (1958); **115**, 1216 (1959).

⁵ H. M. James and A. S. Coolidge, *Phys. Rev.* **49**, 688 (1936).

GENERAL THEORY

In the method of configuration interaction, the state function is approximated as a linear combination of many-electron functions,

$$\Psi = \sum_i c_i \Phi_i, \quad (1)$$

where each of the Φ_i 's (configurations) is an antisymmetrized product of one-electron functions (spin orbitals), and the coefficients c_i are taken as those which minimize the total energy. The total energy for such a function is

$$E = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_{ij} c_i c_j H_{ij}}{\sum_{ij} c_i c_j S_{ij}}, \quad (2)$$

where

$$H_{ij} = \langle \Phi_i | \mathcal{H} | \Phi_j \rangle; \quad S_{ij} = \langle \Phi_i | \Phi_j \rangle.$$

The condition for the energy to be an extremum, $\delta E = 0$, is the well-known matrix eigenvalue equation:

$$\sum_j H_{ij} c_j = E \sum_j S_{ij} c_j. \quad (3)$$

The Hamiltonian used here is the nonrelativistic, spin-independent, infinite-nuclear-mass, Schrödinger Hamiltonian,⁶

$$\mathcal{H} = \sum_n \left(-\frac{\Delta_n}{2} - \frac{Z}{r_n} \right) + \sum_{m < n} \frac{1}{r_{mn}}. \quad (4)$$

It is the eigenvalue of this Hamiltonian which is referred to as the exact energy throughout this paper.

The specific forms of the configurations used for the systems studied here are the following linear combinations of Slater determinants.

2 electrons ($^1S, ^3S$):

$$(\varphi\chi) = [\sqrt{2}\sqrt{D_\lambda}]^{-1} \sum_\mu \times \{ \bar{\varphi}_{\lambda\mu}(1)\alpha\chi_{\lambda\mu}(2)\beta | \pm | \bar{\chi}_{\lambda\mu}(1)\alpha\varphi_{\lambda\mu}(2)\beta | \}.$$

3 electrons (2S):

$$(\varphi\chi)\psi = [(\sqrt{6})\sqrt{D_\lambda}]^{-1} \times \sum_\mu \{ | \bar{\varphi}_{\lambda\mu}(1)\alpha\chi_{\lambda\mu}(2)\beta\psi(3)\alpha | + | \bar{\chi}_{\lambda\mu}(1)\alpha\varphi_{\lambda\mu}(2)\beta\psi(3)\alpha | \}, \quad (5)$$

$$(\varphi\chi)^2 S\psi = [3\sqrt{2}\sqrt{D_\lambda}]^{-1} \times \sum_\mu \{ 2 | \bar{\varphi}_{\lambda\mu}(1)\alpha\chi_{\lambda\mu}(2)\alpha\psi(3)\beta | - | \bar{\varphi}_{\lambda\mu}(1)\alpha\chi_{\lambda\mu}(2)\beta\psi(3)\alpha | - | \psi(1)\alpha\bar{\varphi}_{\lambda\mu}(2)\beta\chi_{\lambda\mu}(3)\alpha | \}.$$

4 electrons (1S):

$$(\psi)^2 \varphi\chi = [4\sqrt{3}(D_\lambda D_{\lambda'})^{\frac{1}{2}}]^{-1} \times \sum_{\mu\mu'} \{ | \bar{\varphi}_{\lambda\mu}(1)\alpha\chi_{\lambda\mu}(2)\beta\bar{\psi}_{\lambda'\mu'}(3)\alpha\psi_{\lambda'\mu'}(4)\beta | + | \bar{\chi}_{\lambda\mu}(1)\alpha\varphi_{\lambda\mu}(3)\beta\bar{\psi}_{\lambda'\mu'}(3)\alpha\psi_{\lambda'\mu'}(4)\beta | \}.$$

The symmetry species of each orbital is labeled by λ , the degeneracy by D_λ , and the subspecies by μ . The bars over the orbitals χ , φ , or ψ indicate the complex

⁶ Unless otherwise specified, atomic units (a.u.) are used throughout this paper. Energy units are 1 a.u. = 27.210 eV, length units are 1 a.u. = 0.52915 Å, and $m_e = \hbar = e = 1$.

conjugate. The phases of the spherical harmonics in these orbitals [see Eq. (6)] are chosen such that $\bar{Y}_{\lambda,\mu} = Y_{\lambda,-\mu}$. Summing over the subspecies μ from $-\lambda$ to $+\lambda$ then yields the S state appropriate for each case. The minus sign in the two-electron functions, of course, is for the 3S state. The two types of configurations that can be constructed for the three-electron case are linearly independent and correspond respectively to a 1S and 3S coupled K shell. Two such functions could have been constructed for the four-electron case if four distinct orbitals had been used. However, for simplicity of the computer programming and because the approximation used was expected to be adequate, the four-electron configurations were always constructed with at least one of the orbitals doubly occupied.

The basis set of one-electron functions chosen consisted of the normalized Slater-type orbitals defined by

$$\chi_{nlm} = \frac{(2\zeta)^{n+\frac{1}{2}}}{[(2n)!]^{\frac{1}{2}}} r^{n-1} e^{-\zeta r} Y_{l,m}(\theta, \varphi). \quad (6)$$

While the nonorthogonality of this set of functions would rapidly make it impracticable with increasing numbers of electrons, the problem was still tractable for four electrons, and the results should remain very nearly the same as if an orthogonalized set were used. If one were to go to still larger systems, it would, no doubt, be necessary to use some orthogonalized set of functions.

1S TWO-ELECTRON SYSTEMS

The lowest 1S state of the helium atom has been studied by numerous authors⁷ using the configuration interaction approach, and it is included here for the sake of completeness as well as a testing ground and starting point for subsequent calculations on larger systems. Since much that can be said about the two-electron 1S state is applicable to the rest of the systems being reported on, it will be dwelt on to some extent. The set of s -functions that was finally settled on is $1s, 2s, 1s', 2s', 3s'$.⁸ Except for the added $3s'$ function, this is the same basis set as was needed for the helium Hartree-Fock function.⁹ Even the ζ 's were fairly similar ($\zeta = 1.48, 3.7$, as opposed to $1.4, 3.0$ for the Hartree-Fock, $\zeta_s < \zeta'_s$). All possible configurations (15) that could be made from these s -functions were included in the wave function. The ζ 's were determined by straight-

forward numerical minimization of the energy over a two-dimensional ζ -grid.

The above basis set was settled on only after a fair amount of numerical experimentation. The set $1s, 2s, 3s, \dots, ns$ with a single ζ reproduced, of course, the results of Holøien and Shull and Löwdin. Independent variation of the ζ 's in this set, as well as the set $1s, 1s', 2s'', 3s'', \dots, ns''$, was tried but soon abandoned, in view of the ratio of paucity of results to amount of labor required for the ζ variation—a ratio that seemed to approach zero rather rapidly. One also runs into problems of linear dependence and multiple minima with a large number of nonlinear parameters.

As the results indicate (Tables II and III), it is necessary to add in higher angular configurations (np^2, nd^2 , etc.) to account for most of the correlation error. As with the s functions, a "double ζ " set of p functions was found to be the best compromise between amount of labor and accuracy of results—the final set being $2p, 3p, 2p', 3p'$. All possible configurations (10) of these functions were added to the s -function substructure. Single ζ sets of each symmetry were used for all higher angular configurations, since their contributions are small and become negligibly different from multiple ζ sets. The ζ 's were optimized numerically in a progressive fashion by holding all lower l -value terms fixed—a procedure that was verified by a few spot checks which reminimized the lower set.

The upshot of all of this is the following 35-configuration function put forward as an approximation to the lowest 1S state of helium.

$$^1\Psi_{2E} = \{1s, 2s, 1s', 2s', 3s'\} + \{2p, 3p, 2p', 3p'\} \\ + \{3d, 4d, 5d\} + \{4f, 5f\} + \{5g\}. \quad (7)$$

The bracket notation here is shorthand for a linear combination (variationally determined coefficients) of all possible configurations that can be made from the functions in the bracket, e.g.,

$$\{3d, 4d, 5d\} \equiv c_1(3d)^2 + c_2(3d4d) + c_3(4d)^2 \\ + c_4(3d5d) + c_5(4d5d) + c_6(5d)^2.$$

This type of function determined for helium was also applied to the isoelectronic series of ions for Z ranging from 1 through 8 (Table I). The ζ 's were optimized along the entire series by straightforward minimization at a few selected points, with the remaining points being read off from the resulting ζ vs Z curves. No doubt, better results could have been obtained in different regions of the isoelectronic series by adjusting the basis set. However, this procedure was not followed, partly to avoid the extra work, and partly to insure some consistently uniform behavior along the series, which is of importance for estimating the error for the negative-ion end of the series. In particular, it should be noted that the error in the total energy decreases with decreasing Z , taking a rather sharp dip at H^- (see Table I). This is a trend which appears to be quite

⁷ G. R. Taylor and R. G. Parr, Proc. Natl. Acad. Sci. U. S. 38, 154 (1952); H. Shull and P. Löwdin, J. Chem. Phys. 30, 617 (1959); E. Holøien, Phys. Rev. 104, 1301 (1956); D. H. Tycko, L. H. Thomas, and K. M. King, *ibid.* 109, 369 (1958); R. K. Nesbet and R. E. Watson, *ibid.* 110, 1073 (1958).

⁸ Priming on functions of the same symmetry refers to different values of ζ , e.g., $1s, 2s, 1s', 1s''$ means a set of Slater type orbitals with exponentials of $\zeta_{1s} = \zeta_{2s} \neq \zeta_{1s'} \neq \zeta_{1s''}$. To avoid an overly cumbersome notation, this convention is not adhered to when going to a different symmetry, e.g., $2p$ is understood to have a different ζ than ns .

⁹ C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Revs. Modern Phys. 32, 186 (1960).

TABLE I. 1S two-electron systems—35 configurations.

Z	1	2	3	4	5	6	7	8
Energies								
Computed	-0.52751	-2.90320	-7.27924	-13.65481	-22.03016	-32.40540	-44.78057	-59.15570
Exact ^a	-0.52775	-2.90372	-7.27991	-13.65557	-22.03097	-32.40625	-44.78145	-59.15660
Error	0.00024	0.00052	0.00067	0.00076	0.00081	0.00085	0.00088	0.00090
ζ^2 s								
ζ_s	0.3	1.48	2.52	3.55	4.56	5.57	6.58	7.6
ζ_s'	1.05	3.7	5.75	7.8	9.85	11.9	14.0	16.0
ζ_p	0.96	2.7	4.45	6.2	7.95	9.7	11.45	13.2
ζ_p'	1.8	5.4	8.9	12.4	15.9	19.4	22.9	26.4
ζ_d	1.9	4.5	7.2	10.0	12.8	15.5	18.3	21.0
ζ_f	2.3	5.2	8.2	11.2	15.2	18.2	21.2	24.2
ζ_g	2.5	6.2	9.9	13.6	17.3	21.0	24.7	28.4
Coefficients.								
$1s^2$	0.09243	0.30709	0.51545	0.52909	0.46506	0.32657	0.23469	0.16845
$1s2s$	-0.08983	-0.58623	-0.76338	-0.77925	-0.74102	-0.64641	-0.59240	-0.54611
$2s^2$	0.02180	0.14117	0.15375	0.14548	0.13445	0.11446	0.10398	0.09318
$1s1s'$	-0.75813	-0.59306	-0.74523	-0.77651	-0.75189	-0.67076	-0.61327	-0.57454
$2s1s'$	0.08886	0.12052	0.19361	0.21295	0.21196	0.18788	0.17385	0.16146
$1s^2$	-0.01312	0.07324	0.10743	0.11900	0.11866	0.10760	0.09914	0.09423
$1s2s'$	0.05199	-0.29466	-0.39384	-0.41769	-0.40700	-0.36513	-0.33476	-0.31444
$2s2s'$	-0.04463	0.05457	0.10211	0.11532	0.11571	0.10329	0.09582	0.08933
$1s^2 2s'$	-0.12684	0.05529	0.10123	0.11853	0.12075	0.11070	0.10271	0.09828
$2s^2$	0.20378	0.07434	0.07174	0.06726	0.06176	0.05472	0.04915	0.04569
$1s3s'$	-0.22838	-0.55471	-0.64785	-0.63526	-0.59439	-0.51865	-0.46881	-0.42973
$2s3s'$	0.10745	0.16365	0.19433	0.18946	0.17777	0.15280	0.13866	0.12536
$1s^2 3s'$	-0.05400	0.14812	0.19574	0.20199	0.19356	0.17141	0.15587	0.14483
$2s^2 3s'$	-0.25226	-0.00026	0.04921	0.06600	0.06968	0.06365	0.05950	0.05659
$3s^2$	0.15331	0.14627	0.14061	0.12579	0.11181	0.09605	0.08522	0.07687
$2p^2$	0.53318	0.34907	0.25757	0.20137	0.16481	0.13932	0.12053	0.10626
$2p3p$	-0.48239	-0.38838	-0.29719	-0.23589	-0.19469	-0.16542	-0.14361	-0.12693
$3p^2$	0.14328	0.14147	0.11023	0.08811	0.07300	0.06216	0.05405	0.04782
$2p2p'$	-0.12255	-0.08323	-0.06365	-0.05043	-0.04156	-0.03528	-0.03061	-0.02703
$3p2p'$	0.06364	0.05171	0.04059	0.03252	0.02696	0.02297	0.01998	0.01768
$2p^2$	0.03555	0.01409	0.00948	0.00714	0.00572	0.00478	0.00410	0.00359
$2p3p'$	-0.48351	-0.24336	-0.17516	-0.13560	-0.11039	-0.09303	-0.08029	-0.07068
$3p3p'$	0.22807	0.12920	0.09531	0.07461	0.06113	0.05172	0.04476	0.03949
$2p^2 3p'$	0.16493	0.01274	0.01129	0.00939	0.00793	0.00683	0.00599	0.00533
$3p^2$	0.15965	0.06653	0.04530	0.03425	0.02752	0.02300	0.01974	0.01730
$3d^2$	0.05073	0.03533	0.02423	0.01796	0.01426	0.01200	0.01023	0.00901
$3d4d$	-0.16718	-0.11962	-0.08301	-0.06216	-0.04967	-0.04182	-0.03577	-0.03150
$4d^2$	0.17595	0.13109	0.09238	0.07000	0.05633	0.04748	0.04075	0.03589
$3d5d$	0.08481	0.06117	0.04287	0.03244	0.02609	0.02197	0.01885	0.01660
$4d5d$	-0.20000	-0.15148	-0.10801	-0.08280	-0.06709	-0.05656	-0.04871	-0.04289
$5d^2$	0.06998	0.05356	0.03870	0.03006	0.02455	0.02070	0.01790	0.01575
$4f^2$	0.01448	0.01137	0.00817	0.00633	0.00463	0.00397	0.00348	0.00309
$4f5f$	-0.02709	-0.02110	-0.01522	-0.01181	-0.00893	-0.00763	-0.00666	-0.00590
$5f^2$	0.01680	0.01295	0.00939	0.00731	0.00573	0.00488	0.00424	0.00375
$5g^2$	0.00177	0.00127	0.00091	0.00070	0.00057	0.00048	0.00041	0.00036

^a See reference 4.

general and is the exact opposite of the behavior of isoelectronic series SCF calculations.⁹ It will show up in all the other systems studied in this research.

This entire calculation was repeated for a smaller (20-configuration) wave function, which was used as a starting point for the four-electron atoms and ions. The 35-configuration function was used as the K shell starting point for the three-electron systems.

As a side interest, some attempts were made to pin down for helium the limiting values of the energy improvements arising from the addition of each class of angular configurations. This was done by adding a successively larger single- ζ set of functions to the lower angular substructure of the final 35-configuration function (see Table III). ΔE_∞ was obtained by extrapolating

 TABLE II. Breakdown of 1S two-electron calculations (35 configurations).

Z	1	2	3	8
Hartree-Fock ^a	-0.48793	-2.86168	-7.23641	-59.11114
S^b	-0.51439	-2.87896	-7.25242	-59.12595
$S+P$	-0.52647	-2.90039	-7.27575	-59.15130
$S+P+D$	-0.52730	-2.90258	-7.27845	-59.15467
$S+P+D+F$	-0.52747	-2.90307	-7.27908	-59.15549
$S+P+D+F+G$	-0.52751	-2.90320	-7.27924	-59.15570
Exact ^c	-0.52775	-2.90372	-7.27991	-59.15660

^a See reference 9.

^b The notation here is $S = \{1s, 2s, 1s', 2s', 3s'\}$, $P = \{2p, 3p, 2p', 3p'\}$, $D = \{3d, 4d, 5d\}$, $F = \{4f, 5f\}$, $G = \{5g\}$.

^c See reference 4.

ΔE . The s -function limit has been determined already by Shull and Löwdin⁷ to be -2.87900 a.u., giving an

TABLE III. Helium angular limit study.

	E	ΔE	ζ
S^a	-2.87896		
$S+\{2p\}$	-2.89839	0.01943	2.41
$S+\{2p,3p\}$	-2.90002	0.02106	2.9
$S+\{2p,3p,4p\}$	-2.90026	0.02130	3.2
$S+\{2p,3p,4p,5p\}$	-2.90037	0.02141	3.5
$S+\{2p,3p,4p,5p,6p\}$	-2.90042	0.02146	3.7
	Limit $\Delta E_\infty=0.02150\pm 0.00001$		
$S+P^a$	-2.90039		
$S+P+\{3d\}$	-2.90216	0.00177	3.6
$S+P+\{3d,4d\}$	-2.90250	0.00211	4.1
$S+P+\{3d,4d,5d\}$	-2.90258	0.00219	4.5
$S+P+\{3d,4d,5d,6d\}$	-2.90262	0.00223	4.8
	Limit $\Delta E_\infty=0.00225\pm 0.00001$		
$S+P+D^a$	-2.90258		
$S+P+D+\{4f\}$	-2.90297	0.00039	4.8
$S+P+D+\{4f,5f\}$	-2.90307	0.00049	5.2
$S+P+D+\{4f,5f,6f\}$	-2.90311	0.00053	5.6
	Limit $\Delta E_\infty\approx 0.00056$		

^a $S = \{1s, 2s, 1s', 2s', 3s'\}$, $P = \{2p, 3p, 2p', 3p'\}$, $D = \{3d, 4d, 5d\}$. These are the same sets of configurations (ζ 's) as in the 35-configuration function of Eq. (7).

energy increment over the Hartree-Fock for s functions of 0.01732.

The necessity of higher angular terms and their slow convergence can be understood in terms of the singular behavior that the eigenfunction must have as $r_{12} \rightarrow 0$.¹⁰ It can be shown that the eigenfunction should have a cusp-like behavior at $r_{12}=0$ such that

$$\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{12}} \right)_{r_{12}=0} = \frac{1}{2},$$

and piling up higher and higher (s, p, d, \dots) angular terms is attempting to represent the details of this behavior much like representing a sawtooth function by a Fourier series (Table II). To some extent, at least, the convergence of the energy with such functions is an indication of how important, energetically, the details of this cusp are. As might be expected from the increasing spatial compactness of the wave functions, these angular terms become more and more important for large Z .

As is clear from the results, the configuration interaction procedure is slowly converging from the standpoint of reaching a particular limit as well as of how

far along the angular series one must go. This investigation terminated at 35 configurations, through g functions. It is clear that one could slowly approach the eigenvalue by adding more configurations and higher angular terms (h, i, \dots , etc.), but it was felt that the point of diminishing returns had been reached if not, indeed, passed. The results are discouraging if one is looking for Pekeris-type accuracy, however they are somewhat encouraging in terms of somewhat larger systems where one might settle for a reasonable compromise between accuracy and simplicity.

³S TWO-ELECTRON SYSTEMS

A similar search for a configuration interaction basis set was made for the lowest ³S state of helium. This search did not need to be as exhaustive as for the ¹S state, since the orbital product approximation is quite good to begin with. Putting the two electrons in spatially different functions and with parallel spins already has the effect of crudely representing the "way the electrons tend to avoid each other." Configuration interaction here, then, is simply a way of representing the still finer details of the eigenfunction.

The function finally settled on as an approximation to the eigenfunction is the following 19-configuration function:

$${}^3\Psi_{2E} = [1s, 2s, 3s, 1s', 2s'] + [2p, 3p, 2p', 3p'] + [3d, 4d, 3d']. \quad (8)$$

The square bracket notation here means a linear combination of all possible triplet combinations of the enclosed orbitals, e.g.,

$$[3d, 4d, 3d'] \equiv c_1(3d4d - 4d3d) + c_2(3d3d' - 3d'3d) + c_3(4d3d' - 3d'4d).$$

The doubling of the ζ 's here has perhaps a little more physical significance in that they correspond roughly to the two different electrons.

As with the ¹S state, once helium was settled, this function was applied to the isoelectronic series through $Z=8$, keeping the same form of the function but minimizing with respect to the ζ 's along the series. The error trend along the series (see Table V) is not as obvious as in all the other calculations. The correct Schrödinger energy for helium is taken from Pekeris (second paper in reference 3).

A rough estimate of the nonrelativistic Schrödinger energy of the rest of the isoelectronic series was made by adding to the Schrödinger one-electron atom energy the relativistically adjusted experimental ionization energy.¹¹ This adjustment was made by looking at the experimental $2s$ ionization energy as the energy of a one-electron atom in the $2s^2S$ state and applying the

¹⁰ C. C. J. Roothaan and A. W. Weiss, Revs. Modern Phys. **32**, 194 (1960).

¹¹ *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

TABLE IV. 1S two-electron systems—20 configurations.

Z	1	2	3	4	5	6	7	8
Energies								
Computed	-0.52707	-2.90270	-7.27862	-13.65412	-22.02943	-32.40464	-44.77979	-59.15490
Exact ^a	-0.52775	-2.90372	-7.27991	-13.65557	-22.03097	-32.40625	-44.78145	-59.15660
Error	0.00068	0.00102	0.00129	0.00145	0.00154	0.00161	0.00166	0.00170
ζ 's								
ζ_s	0.45	1.52	2.55	3.6	4.62	5.65	6.68	7.7
$\zeta_{s'}$	1.1	3.3	5.4	7.4	9.4	11.4	13.4	15.4
ζ_p	0.85	2.4	3.95	5.5	7.05	8.6	10.1	11.7
$\zeta_{p'}$	1.2	4.3	7.1	9.7	12.3	14.8	17.4	20.0
ζ_d	1.7	4.1	6.5	8.9	11.3	13.7	16.1	18.5
ζ_f	1.8	4.7	7.6	10.5	14.2	17.0	20.0	23.0
Coefficients								
$1s^2$	0.36392	0.33482	0.11236	0.03996	-0.06489	-0.13554	-0.19161	-0.24264
$1s2s$	-0.36241	-0.72953	-0.61207	-0.56969	-0.49185	-0.44032	-0.39922	-0.36099
$2s^2$	0.08739	0.18820	0.15048	0.12823	+0.10725	0.09247	0.08107	0.07181
$1s1s'$	-0.73912	-0.69063	-0.53776	-0.48704	-0.41996	-0.37138	-0.33207	-0.29750
$2s1s'$	-0.15100	0.16905	0.15519	0.14867	0.13085	0.11703	0.10532	0.09476
$1s'^2$	0.06447	0.10337	0.08417	0.07955	0.06977	0.06245	0.05629	0.05066
$1s2s'$	-0.47403	-0.60201	-0.46916	-0.41584	-0.35556	-0.31176	-0.27696	-0.24737
$2s2s'$	0.13327	0.17657	0.14584	0.13187	0.11365	0.09997	0.08893	0.07955
$1s'2s'$	0.05506	0.16481	0.13646	0.12821	0.11200	0.09977	0.08958	0.08048
$2s'^2$	0.18344	0.13980	0.10270	0.08755	0.07384	0.06400	0.05639	0.05015
$2p^2$	0.29026	0.09325	0.06786	0.05598	0.04736	0.04191	0.03581	0.03270
$2p2p'$	-0.06097	-0.01985	-0.01524	-0.01397	-0.01253	-0.01184	-0.01007	-0.00958
$2p'^2$	0.08194	0.01919	0.01186	0.00927	0.00761	0.00663	0.00568	0.00506
$2p3p'$	-0.44443	-0.08940	-0.06569	-0.05604	-0.04823	-0.04349	-0.03722	-0.03425
$2p'3p'$	-0.04428	-0.01867	-0.01049	-0.00674	-0.00476	-0.00337	-0.00295	-0.00216
$3p'^2$	0.25885	0.05922	0.04043	0.03287	0.02755	0.02428	0.02084	0.01877
$3d^2$	0.02952	0.02009	0.01413	0.01083	0.00877	0.00737	0.00635	0.00557
$3d4d$	-0.04880	-0.03432	-0.02432	-0.01871	-0.01518	-0.01276	-0.01100	-0.00967
$4d^2$	0.03231	0.02344	0.01673	0.01292	0.01051	0.00884	0.00763	0.00671
$4f^2$	0.00441	0.00299	0.00210	0.00161	0.00122	0.00104	0.00090	0.00079

^a See reference 4.

well-known relation from Dirac theory:

$$E_{\text{Dirac}} = E_{\text{Sch}} \left[1 + \left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right) \frac{\alpha^2 (Z - \sigma)^2}{n} \right], \quad (9)$$

where j is the angular momentum quantum number of the electron, n the principal quantum number, and α the fine structure constant. The shielding σ was chosen as that which made the helium value agree with Pekeris' value. The experimental error is indicated in parenthesis in Table V and is, no doubt, responsible for the fluctuations in the computed-energy error.

A fairly extensive search was also made for a bound 3S state of H^- , without success. The procedure followed for varying the ζ pairs consisted of computing the energy over a two-dimensional ζ grid until a minimum was located and then homing in on the bottom of the well. For H^- , however, the energies remained unbound but gradually sloped down to -0.5 a.u. as $\zeta_s \rightarrow 1.0$ and $\zeta_{s'} \rightarrow 0$, with no sign of a minimum, as though the Slater-type orbitals were trying to look like a bound H-atom function plus a free electron. Since the accuracy for the neutral system (helium) was 0.00002 a.u., it seems reasonable to assume that if H^- were bound by this much it could have been picked up by the 19-configuration function. It appears, therefore, that if the

H^- 3S state is stable, it is bound by no more than 0.0005 ev.

2S THREE-ELECTRON SYSTEMS

The ground state of lithium has been treated to some extent by several authors in the configuration interaction approximation—Holøien's work coming closest to the present treatment.¹² It has also been computed with a 12-term function explicitly containing r_{ij} by James and Coolidge.⁵ The interest here is in extending the entire approach described for the two-electron systems to a system with an extra outer electron.

The starting point for this system is the 35-configuration function for the 1S two-electron ion. The first 35 configurations of the lithium wave function then are simply the K -shell configurations of Li^+ , each multiplied by a $2s$ Slater-type function and properly antisymmetrized. The coefficients are freely determined by the variational principle, but the K -shell configurations and ζ values were taken over from the Li^+ ion.¹³ The problem then boils down to finding the best set of

¹² E. Holøien, Kgl. Norske Videnskab. Selskabs, Forh. **31**, 6 (1958).

¹³ A simple example should serve to clarify this. If the two-electron 1S state is represented by the function $K = 1s^2 + 1s2s + 2s^2$, then the first 3 configurations of the three-electron 2S state would be $K \cdot 2s' = 1s^2 2s' + 1s2s2s' + 2s^2 2s'$.

TABLE V. 3S two-electron systems—19 configurations.

Z	2	3	4	5	6	7	8
Energies							
Computed	-2.17521	-5.11069	-9.29713	-14.73385	-21.42071	-29.35763	-38.54459
Exact ^a	-2.17523	-5.11073	-9.29713	-14.73402	-21.42105	-29.35792	-38.54448
Error	0.00002	(±0.00001)	(±0.00046)	(±0.00091)	(±0.00137)	(±0.00228)	(±0.00273)
ζ 's							
ζ_s	1.75	2.6	3.5	4.4	5.25	6.1	7.0
ζ'_s	0.61	1.12	1.63	2.13	2.64	3.15	3.65
ζ_p	2.6	4.0	5.4	6.8	8.2	9.6	11.0
ζ'_p	1.25	2.1	3.0	3.9	4.75	5.6	6.5
ζ_d	2.8	4.2	5.5	6.8	8.2	9.5	10.9
ζ'_d	1.8	2.9	4.0	5.1	6.2	7.3	8.4
Coefficients							
$1s2s' - 2s'1s$	1.30806	1.55467	1.70765	1.76117	1.88502	1.98305	1.99093
$2s2s' - 2s'2s$	-0.33058	-0.42016	-0.42775	-0.41916	-0.46051	-0.49118	-0.47697
$3s2s' - 2s'3s$	0.07243	0.11369	0.11854	0.11622	0.13406	0.14610	0.13824
$1s'2s' - 2s'1s'$	-0.01855	-0.05061	-0.06182	-0.06672	-0.09046	-0.10987	-0.10580
$1s1s' - 1s'1s$	0.01283	-0.02350	-0.49505	-0.58253	-0.77519	-0.93849	-0.96373
$2s1s' - 1s'2s$	0.03300	0.13419	0.20753	0.22429	0.28209	0.32687	0.31993
$3s1s' - 1s'3s$	-0.03446	-0.09254	-0.12578	-0.13468	-0.15927	-0.17395	-0.16660
$1s3s - 3s1s$	-0.04515	-0.04871	-0.04463	-0.04851	-0.04461	-0.04007	-0.03948
$2s3s - 3s2s$	-0.01374	-0.03433	-0.04724	-0.04827	-0.05500	-0.05822	-0.05447
$1s2s - 2s1s$	-0.08650	-0.08298	-0.03856	-0.03272	0.00561	0.03965	0.03720
$2p3p' - 3p'2p$	-0.00499	-0.00248	-0.00008	0.00154	0.00191	0.00207	0.00254
$3p3p' - 3p'3p$	0.01891	0.02641	0.02888	0.02888	0.02661	0.02445	0.02335
$2p'3p' - 3p'2p'$	-0.03845	-0.04549	-0.04908	-0.04890	-0.04435	-0.04036	-0.03873
$2p2p' - 2p'2p$	0.01213	0.01521	0.01661	0.01651	0.01493	0.01356	0.01295
$3p2p' - 2p'3p$	-0.04038	-0.04718	-0.04808	-0.04661	-0.04268	-0.03908	-0.03698
$2p3p - 3p2p$	-0.01369	-0.01677	-0.01820	-0.01829	-0.01684	-0.01548	-0.01490
$3d3d' - 3d'3d$	0.00562	0.00678	0.00764	0.00798	0.00730	0.00727	0.00662
$4d3d' - 3d'4d$	-0.01394	-0.01535	-0.01620	-0.01623	-0.01469	-0.01429	-0.01296
$3d4d - 4d3d$	-0.00824	-0.01010	-0.01151	-0.01204	-0.01099	-0.01093	-0.00994

^a For sources of exact values, see text preceding Eq. (9).

extra "mixing" configurations which, in part at least, represents some of the details of the correlation between the K shell and the outer $2s$ electron. While one can think of these configurations in this way, it is not entirely correct, since the Slater $2s$ function is nodeless and they are also acting to put a loop in the outer electron orbital.

The search for the best extra terms was a straightforward, tedious, numerical task, which resulted in the following 45-configuration function as an approximation to the 3S three-electron eigenfunction.

$${}^3\Psi_{3E} = K \cdot 2s'' + \Phi_1 + \Phi_2, \quad (10)$$

where

$$\begin{aligned} \Phi_1 = & (1s)^2 1s'' + (1s1s') 1s'' + (2p)^2 1s'' \\ & + (1s)^2 2s + (2p'')^2 1s + (3d'')^2 1s, \\ \Phi_2 = & (3p2p'')^3 S1s + (2p''3p'')^3 S1s \\ & + (5d3d'')^3 S1s + (2p''3p'')^3 S2s. \end{aligned} \quad (11)$$

The configurations like $(3p2p'')^3 S1s$ are the triplet coupled K -shell terms mentioned earlier, and the exact form of the configuration is the second of the three-electron functions of Eqs. (5). It is interesting to see from Table VI that their contribution is not negligible. Also, they all contain two higher angular functions. It is tempting to think of Φ_1 as representing largely the correlation between the outer electron and the inner

one of opposite spin, and Φ_2 the correlation between the outer electron and the inner one of the same spin. However, this may be stretching the imagination too much. Several spot checks were made on the K -shell ζ 's by re-minimizing them for the lithium atom holding the outer electron ζ 's constant, with the result that they remained substantially unchanged.

With regard to looking at the K shell in this way, as a somewhat autonomous structure, it is interesting to observe the energy improvements as successively higher angular terms are added to it, starting with only s -type K configurations. These results for Li and Be^+ are shown in Table VII and compared with the corresponding two-electron ion. The comparison is, to say the least, striking.

TABLE VI. Lithium ground-state energies.

Hartree-Fock ^a	-7.43273
Holøien ^b	-7.47050
James and Coolidge ^c	-7.47608
$K \cdot 2s''^d$	-7.47402
$K \cdot 2s'' + \Phi_1$	-7.47622
$K \cdot 2s'' + \Phi_1 + \Phi_2$	-7.47710
Exact ^e	-7.47807

^a See reference 9.

^b See reference 12.

^c See reference 5.

^d For definitions see Eqs. (10) and (11) of text.

^e For derivation of the exact value, see text preceding equation (9) and the discussion of 3S two-electron systems.

TABLE VII. Breakdown of *K*-shell energy contributions.

	Two-electron 1S			<i>E</i>	Be^{++}	ΔE
	<i>E</i>	Li^+	ΔE			
S^a	-7.25242			-13.62678		
$S+P$	-7.27575		0.02333	-13.65096		0.02418
$S+P+D$	-7.27845		0.00270	-13.65393		0.00297
$S+P+D+F$	-7.27908		0.00063	-13.65464		0.00071
$S+P+D+F+G$	-7.27924		0.00016	-13.65481		0.00017
	Three-electron 2S			<i>E</i>	Be^+	ΔE
	<i>E</i>	Li	ΔE			
$S \cdot 2s''$	-7.44720			-14.28639		
$(S+P) \cdot 2s''$	-7.47054		0.02334	-14.31047		0.02408
$(S+P+D) \cdot 2s''$	-7.47323		0.00269	-14.31342		0.00295
$(S+P+D+F) \cdot 2s''$	-7.47386		0.00063	-14.31411		0.00069
$(S+P+D+F+G) \cdot 2s''$	-7.47402		0.00016	-14.31429		0.00018
$(S+P+D+F+G) \cdot 2s'' + \Phi_1^b$	-7.47622		0.00220	-14.32211		0.00782
$(S+P+D+F+G) \cdot 2s'' + \Phi_1 + \Phi_2$	-7.47710		0.00088	-14.32350		0.00139

^a The notation is $S = \{1s, 2s, 1s', 2s', 3s'\}$, $P = \{2p, 3p, 2p', 3p'\}$, $D = \{3d, 4d, 5d\}$, $F = \{4f, 5f\}$, $G = \{5g\}$.
^b See Eq. (11) in text for definitions.

Having settled on this function for lithium, it was applied to the series of isoelectronic ions through $Z=8$, optimizing the ζ 's and, of course, coefficients along the series (Table VIII). The energies given as the exact Schrödinger eigenvalues in Table VIII were estimated from experimental data¹¹ by adding to the Pekeris two-electron ion energy the observed $2s$ ionization energy, relativistically corrected. Relativistic corrections were estimated by treating the observed ionization energy as the energy of a shielded Dirac $2s$ electron with Slater shielding. The error trend mentioned previously should be noted.

An attempt was made to obtain binding for the 2S state of He^- , without success. An effect similar to that for the $\text{H}^- {}^3S$ state was found here also. In varying the outer electron ζ , the energy remained above the computed value for helium but gradually approached it as $\zeta_{2s''}$ was decreased, with no sign of a minimum. $\zeta_{2s''}$ was taken down to 0.001, where the energy difference between He and He^- was in the roundoff error. Presuming that He^- could be picked up with an error no greater than that of the lithium calculation, one is led to the conclusion that it is probably unstable, and, if it is stable, it is bound by no more than 0.026 ev.

1S FOUR-ELECTRON SYSTEMS

There have been several configuration interaction studies made of the beryllium atom,^{14,15} but none of the

¹⁴ S. F. Boys, Proc. Roy. Soc. (London) **A217**, 136 (1953).

¹⁵ V. V. Kibartas, V. I. Kavetskis, and A. P. Iutsis, Soviet Phys.—JETP **2**, 491 (1956).

isoelectronic series and only one that is comparable in extent to this research.¹⁶ The approach here is similar to that applied to the lithium atom. For beryllium, the 20-configuration *K*-shell function for Be^{++} was taken as the starting point—the first 20 configurations being simply the *K*-shell functions multiplied by a doubly occupied Slater $2s$ -type orbital, and the whole thing properly antisymmetrized. Once again, the problem came down to a straightforward but tedious search for the best way of representing the *L* shell and the best “mixing” configurations.

The function finally settled on was the following 55-configuration function:

$${}^1\Psi_{4E} = S + P + D + F, \quad (12)$$

where

$$\begin{aligned} S &= K_s \cdot (2s'')^2 + \{1s'', 2s'', 1s'''\} 1s^2 \\ &\quad + (1s''2s + 2s''2s + 1s'''2s) 1s^2 + (1s1s' + 1s2s) 1s'^2 \\ &\quad + (1s''2s'' + 1s'''1s'') 2s^2, \\ P &= K_p \cdot (2s'')^2 \\ &\quad + \{2p, 2p'', 3p'''\} 1s^2 + (1s''2s'' + 1s'''2s'') 2p^2 \\ &\quad + (1s1s' + 1s2s + 2s^2 + 1s2s'' + 2p^2) 2p'^2 \\ &\quad + (1s2s'') 3p'^2, \\ D &= K_D \cdot (2s'')^2 + 3d'^2 1s^2 + (1s''2s'' + 2p'^2) 3d^2 \\ &\quad + (1s2s + 1s2s'' + 2p^2) 3d'^2, \\ F &= K_F \cdot (2s'')^2 + 4f'^2 2s'^2 + (1s''2s'') 4f^2 + (1s2s'') 4f'^2. \end{aligned} \quad (13)$$

The bracket notation is the same as before, and its

¹⁶ R. E. Watson, Phys. Rev. **119**, 170 (1960).

TABLE VIII. 2S three-electron systems—45 configurations.

Z	3	4	5	6	7	8
Energies						
Computed	-7.47710	-14.32350	-23.42312	-34.77384	-48.37509	-64.22661
Exact ^a	-7.47807	-14.32479	-23.42471	-34.77573	-48.37728	-64.22917
Error	0.00097	0.00129	0.00159	0.00189	0.00219	0.00256
ξ 's						
$\xi_s''^b$	0.68	1.20	1.71	2.21	2.72	3.22
ξ_p''	1.65	2.4	3.18	3.9	4.7	5.5
ξ_d'	2.5	3.7	4.9	6.0	7.1	8.2
Coefficients						
(1s) ${}^2s''$	0.39992	0.40003	0.32523	0.18140	0.13862	0.00233
(1s2s) $2s''$	-0.60623	-0.66540	-0.65367	-0.56821	-0.57295	-0.48009
(2s) ${}^2s''$	0.12431	0.12938	0.12521	0.10581	0.10786	0.08751
(1s1s') $2s''$	-0.56973	-0.62625	-0.62099	-0.55195	-0.54864	-0.47383
(2s1s') $2s''$	0.15246	0.17953	0.18423	0.16150	0.16747	0.13980
(1s') ${}^2s''$	0.08061	0.09338	0.09521	0.08621	0.08656	0.07572
(1s2s') $2s''$	-0.30086	-0.33828	-0.33927	-0.30239	-0.30134	-0.26040
(2s2s') $2s''$	0.08111	0.09877	0.10271	0.09019	0.09365	0.07819
(1s'2s') $2s''$	0.07687	0.09495	0.09945	0.09057	0.09185	0.08032
(2s') ${}^2s''$	0.05253	0.05127	0.04837	0.04282	0.04079	0.03591
(1s3s') $2s''$	-0.48815	-0.49523	-0.46735	-0.40310	-0.39320	-0.33242
(2s3s') $2s''$	0.15015	0.15328	0.14566	0.12270	0.12321	0.10049
(1s'3s') $2s''$	0.14625	0.15551	0.15020	0.13190	0.12934	0.11091
(2s'3s') $2s''$	0.03904	0.05410	0.05746	0.05130	0.05288	0.04485
(3s') ${}^2s''$	0.10306	0.09373	0.08336	0.07102	0.06630	0.05659
(2p) ${}^2s''$	0.18931	0.14926	0.12163	0.10237	0.08794	0.07692
(2p3p) $2s''$	-0.21814	-0.17376	-0.14235	-0.12009	-0.10335	-0.09048
(3p) ${}^2s''$	0.08109	0.06519	0.05374	0.04546	0.03926	0.03445
(2p2p') $2s''$	-0.04648	-0.03694	-0.03024	-0.02552	-0.02197	-0.01924
(3p2p') $2s''$	0.02982	0.02400	0.01978	0.01674	0.01445	0.01268
(2p') ${}^2s''$	0.00684	0.00518	0.00415	0.00346	0.00296	0.00258
(2p3p') $2s''$	-0.12709	-0.09859	-0.07978	-0.06687	-0.05732	-0.05010
(3p3p') $2s''$	0.06975	0.05480	0.04461	0.03749	0.03220	0.02815
(2p'3p') $2s''$	0.00836	0.00695	0.00580	0.00495	0.00429	0.00377
(3p') ${}^2s''$	0.03261	0.02473	0.01981	0.01651	0.01412	0.01232
(3d) ${}^2s''$	0.01727	0.01284	0.01021	0.00860	0.00732	0.00645
(3d4d) $2s''$	-0.05913	-0.04428	-0.03533	-0.02972	-0.02536	-0.02232
(4d) ${}^2s''$	0.06571	0.04964	0.03976	0.03342	0.02857	0.02512
(3d5d) $2s''$	0.03058	0.02315	0.01858	0.01563	0.01337	0.01176
(4d5d) $2s''$	-0.07692	-0.05879	-0.04740	-0.03982	-0.03415	-0.02999
(5d) ${}^2s''$	0.02762	0.02144	0.01746	0.01467	0.01264	0.01110
(4f) ${}^2s''$	0.00578	0.00445	0.00324	0.00277	0.00242	0.00215
(4f5f) $2s''$	-0.01071	-0.00822	-0.00617	-0.00524	-0.00454	-0.00401
(5f) ${}^2s''$	0.00658	0.00503	0.00392	0.00330	0.00284	0.00250
(5g) ${}^2s''$	0.00064	0.00049	0.00040	0.00034	0.00029	0.00025
(1s) ${}^21s''$	0.03521	0.11056	0.17003	0.20545	0.24977	0.27268
(1s1s') $1s''$	0.00532	0.00788	0.00810	0.00657	0.00661	0.00529
(1s) 22s	0.01628	0.01529	0.01268	0.01286	0.00885	0.00863
(2p) ${}^21s''$	-0.02050	-0.00269	-0.00254	-0.00232	-0.00208	-0.00184
(2p') 21s	-0.00775	-0.00780	-0.00703	-0.00626	-0.00559	-0.00503
(3d') 21s	-0.00173	-0.00181	-0.00167	-0.00152	-0.00138	-0.00125
(2p'3p') 3S2s	0.00590	0.00324	0.00197	0.00127	0.00091	0.00062
(3p2p') 3S1s	-0.00100	-0.00202	-0.00204	-0.00224	-0.00197	-0.00175
(2p'3p') 3S1s	-0.02878	-0.02200	-0.01753	-0.01402	-0.01208	-0.01054
(5d3d') 3S1s	-0.00143	-0.00151	-0.00140	-0.00127	-0.00114	-0.00104

^a See discussion of 2S three-electron systems in text.

^b The ξ 's for all other functions are the same as for the 1S two-electron (35-configuration) calculations.

meaning here should be clear. K_s , K_p , etc., refer to the corresponding angular configurations of the two-electron function.

The results for this function are shown in Table IX and compared with several other calculations. It is clear that they are not very good when considered with respect to the two- and three-electron calculations. One reason, of course, is the smaller set of K -shell functions used here. Another reason is the limitation of the four electron configurations, as mentioned previously, to always contain at least one doubly occupied orbital. This precluded the use of a whole host of configurations such as $(1s1s')(2p3p)$, etc., as well as the other class of

TABLE IX. Beryllium atom calculations.

Hartree-Fock ^a	-14.57302
Iutsis <i>et al.</i> (3-conf.) ^b	-14.642
Boys (7 conf.) ^c	-14.637
Watson (37 conf.) ^d	-14.65740
S (22 conf.) ^e	-14.59110
$S+P$ (42 conf.)	-14.65722
$S+P+D$ (51 conf.)	-14.66039
$S+P+D+F$ (55 conf.)	-14.66090
Exact ^f	-14.66741

^a See reference 9.

^b See reference 15.

^c See reference 14.

^d See reference 16.

^e For definition of symbols, see Eqs. (12) and (13).

^f See discussion of 1S four-electron systems in text.

triplet coupled K - and L -shell configurations like $(1s1s')^3S(2p3p)^3S$. The latter type of configurations vanish identically unless all four orbitals are different. As demonstrated by the three-electron calculations, their effect is not negligible in terms of the desired accuracy. At the time of writing the computer program, it was thought that, if the electron correlation within each shell could be adequately represented, the inter-

TABLE X. 1S four-electron systems—55 configurations.

Z	3	4	5	6	7	8
Energies						
Computed	-7.49561	-14.66090	-24.34132	-36.52621	-51.21281	-68.40009
Exact ^a	...	-14.66741	-24.34915	-36.53524	-51.22358	-68.41332
Error	...	0.00651	0.00782	0.00902	0.01077	0.01323
ξ's						
$\xi_s''^b$	0.42	0.94	1.44	1.94	2.44	2.94
ξ_s'''	2.0	2.3	2.8	3.3	3.8	4.3
ξ_p''	0.48	1.1	1.8	2.5	3.2	3.9
ξ_d'	0.70	1.3	1.9	2.5	3.1	3.7
ξ_f'	1.5	2.4	3.0	3.6	4.2	4.8
Coefficients						
$(1s)^2(2s'')^2$	0.93351	0.91165	0.87754	0.77289	0.54829	0.05506
$(1s2s)(2s'')^2$	-0.54524	-0.65550	-0.63233	-0.60914	-0.57897	-0.52899
$(2s)^2(2s'')^2$	0.06611	0.12367	0.12968	0.12652	0.11728	0.10141
$(1s1s')(2s'')^2$	-0.49069	-0.54059	-0.50834	-0.47842	-0.44629	-0.40414
$(2s1s')(2s'')^2$	0.15933	0.18505	0.17823	0.17028	0.16019	0.14483
$(1s')^2(2s'')^2$	0.08109	0.08905	0.08400	0.07944	0.07442	0.06759
$(1s2s')(2s'')^2$	-0.45815	-0.46686	-0.42311	-0.38896	-0.35643	-0.31712
$(2s2s')(2s'')^2$	0.15026	0.16153	0.14942	0.13923	0.12857	0.11404
$(1s'2s')(2s'')^2$	0.13274	0.14407	0.13390	0.12539	0.11646	0.10457
$(2s')^2(2s'')^2$	0.09820	0.09360	0.08235	0.07406	0.06686	0.05912
$(1s'')^2(1s)^2$	0.49526	1.02587	1.84495	2.43287	2.14867	-0.68785
$(1s'2s')(1s)^2$	-1.36905	-1.85924	-2.58144	-2.96682	-2.66161	-0.70078
$(1s'1s'')(1s)^2$	-1.42699	-1.61620	-2.93374	-3.60154	-2.60505	3.04377
$(2s'1s'')(1s)^2$	1.69724	1.44396	2.10366	2.37362	2.01148	0.15512
$(1s'')^2(1s)^2$	0.81464	0.69164	1.25315	1.40966	0.78040	-1.95387
$(2s1s'')(1s)^2$	0.34009	0.23693	0.28722	0.16687	-0.13735	-0.77242
$(2s2s'')(1s)^2$	-0.33204	-0.14418	-0.13654	-0.05742	0.07618	0.30639
$(2s1s'')(1s)^2$	-0.23863	-0.18025	-0.24986	-0.16372	0.07609	0.58992
$(1s2s)(1s'')^2$	-0.10678	-0.04860	-0.01808	-0.00101	0.01015	0.01588
$(1s1s')(1s'')^2$	-0.04208	-0.01272	-0.00083	0.00561	0.00958	0.01196
$(1s'2s'')(2s)^2$	0.10895	0.05337	0.03242	0.02482	0.02690	0.03703
$(1s'1s'')(2s)^2$	-0.00846	-0.01537	-0.01488	-0.02081	-0.03191	-0.04811
$(2p)^2(2s'')^2$	0.03977	0.04142	0.03908	0.03799	0.03501	0.03413
$(2p2p')(2s'')^2$	-0.01367	-0.01262	-0.01140	-0.01104	-0.00967	-0.00946
$(2p')^2(2s'')^2$	0.01090	0.00902	0.00754	0.00664	0.00574	0.00513
$(2p3p')(2s'')^2$	-0.05864	-0.05064	-0.04463	-0.04134	-0.03602	-0.03354
$(2p'3p')(2s'')^2$	-0.00983	-0.00713	-0.00527	-0.00376	-0.00314	-0.00220
$(3p')^2(2s'')^2$	0.03671	0.03113	0.02675	0.02398	0.02076	0.01874
$(2p')^2(1s)^2$	0.19593	0.06863	0.01148	-0.00457	-0.01002	-0.01143
$(2p'3p'')(1s)^2$	-0.04896	0.07103	0.09406	0.08487	0.07394	0.06574
$(3p'')^2(1s)^2$	0.01897	0.02293	0.05472	0.07438	0.08595	0.09239
$(2p2p'')(1s)^2$	0.00030	-0.00226	-0.00184	-0.00103	-0.00047	-0.00006
$(2p3p'')(1s)^2$	0.00199	0.00482	0.00639	0.00778	0.00911	0.00997
$(2p)^2(1s)^2$	-0.00001	0.00034	0.00061	0.00071	0.00074	0.00073
$(1s'2s'')(2p)^2$	0.02542	0.01502	0.01078	0.00734	0.00431	0.00117
$(1s'1s'')(2p)^2$	-0.00786	-0.01021	-0.01002	-0.00880	-0.00719	-0.00509
$(1s1s')(2p'')^2$	0.03643	0.02425	0.01799	0.01449	0.01222	0.01056
$(1s2s)(2p'')^2$	0.07606	0.05941	0.04644	0.04050	0.03669	0.03319
$(2s)^2(2p'')^2$	-0.03591	-0.02228	-0.01525	-0.01152	-0.00926	-0.00774
$(1s2s'')(2p'')^2$	-0.00537	-0.01606	-0.02015	-0.02028	-0.01929	-0.01798
$(2p)^2(2p'')^2$	-0.00951	-0.00616	-0.00443	-0.00343	-0.00281	-0.00235
$(1s2s'')(3p'')^2$	0.00481	0.01173	0.01293	0.01192	0.01065	0.00941
$(3d)^2(2s'')^2$	0.01036	0.01071	0.00958	0.00848	0.00756	0.00679
$(3d4d)(2s'')^2$	-0.02215	-0.01766	-0.01428	-0.01191	-0.01018	-0.00887
$(4d)^2(2s'')^2$	0.01518	0.01199	0.00960	0.00793	0.00672	0.00582
$(3d')^2(1s)^2$	0.01182	0.01320	0.01140	0.00973	0.00844	0.00748
$(1s'2s'')(3d)^2$	0.00298	-0.00033	-0.00122	-0.00152	-0.00160	-0.00159
$(1s2s)(3d')^2$	-0.00189	-0.00105	-0.00051	-0.00010	0.00014	0.00025
$(1s2s'')(3d')^2$	-0.00047	-0.00121	-0.00164	-0.00183	-0.00187	-0.00185
$(3d)^2(2p'')^2$	-0.00176	-0.00118	-0.00086	-0.00067	-0.00055	-0.00046
$(3d')^2(2p)^2$	-0.00043	-0.00037	-0.00026	-0.00019	-0.00014	-0.00011
$(4f)^2(2s'')^2$	0.00090	0.00172	0.00160	0.00154	0.00143	0.00131
$(4f')^2(2s'')^2$	0.00012	0.00017	0.00010	0.00004	0.00000	-0.00002
$(1s'2s'')(4f)^2$	0.00118	-0.00021	-0.00049	-0.00063	-0.00065	-0.00065
$(1s2s'')(4f')^2$	-0.00087	-0.00081	-0.00034	-0.00005	0.00013	0.00025

^a See discussion of 1S four-electron systems in text.

^b All other functions are the same as for the 1S two-electron (20-configuration) calculations.

shell effects could be handled satisfactorily in a somewhat sloppy fashion. It seems reasonable also to presume that a beryllium wave function that is as accurate as the 45-configuration lithium function should contain, roughly at least, twice as many configurations. In this regard, comparison of the 55-configuration energy with Watson's (a 37-configuration function) and Boys' (7 configurations) shows just about what one might expect. The results also illustrate the importance of the p -function orbital degeneracy pointed out by Watson¹⁶ and Nesbet.¹⁷

The isoelectronic series through $Z=8$ was also done for the four-electron 1S ions in the same way as the two- and three-electron systems (Table X). The same wave function was used as for beryllium, optimizing the ζ 's along the series. The same error trend displayed by the other systems also shows up here, the accuracy increasing towards the negative end of the series. A remark is in order concerning the estimated "exact" total energies. They were computed by adding to the Pekeris two-electron ion energy the relativistically corrected experimental first and second $2s$ ionization energies. The second ionization energy was corrected in the same way as described under the three-electron systems. The first ionization energy was corrected by applying the Breit equation corrections for a shielded hydrogenic $2s^2$ configuration, with Slater shielding.

The negative lithium ion, in particular, merits some discussion. Since this is a variational calculation, the computed energy of -7.49561 a.u. represents an upper bound to the eigenvalue. Comparing with the exact value for neutral lithium yields a lower bound to the electron affinity of 0.4773 ev. If one assumes that the computed Li^- energy is in error by the same amount as beryllium, a value of -7.50212 a.u. would be assigned to the energy eigenvalue, corresponding to an electron affinity of about 0.65 ev. In view of the error trend in these isoelectronic series calculations, it seems reasonable to take this as an approximate upper limit to the electron affinity. Least-squares fitting of a cubic to the errors in the isoelectronic series extrapolates to an error of 0.00509 a.u. in the computed Li^- energy. This yields a probable value for the electron affinity of approximately 0.62 ev.

CONCLUSIONS

It appears clear that, in summary, one can say that trying to obtain very accurate wave functions by configuration interaction rapidly becomes a case of hopelessly diminishing returns. All of the results of this research could easily have been improved on simply by

adding more configurations or perhaps by further experimenting with the types of configurations, but it is clear that the improvements would have been small, and one would eventually converge on the correct energy only by small bits at a time. If something approaching Hylleraas or Pekeris type accuracy is desired for systems with more than two electrons, one will have to go to outrageously long expansions, probably too long for present day equipment. It is possible to obtain a sizable improvement over Hartree-Fock functions for larger systems with relatively simple functions, as has been demonstrated by Boys on beryllium and various authors on helium-like systems, but picking up the remaining discrepancy is a long and tedious task which appears to be simply out of range.

There are two directions that can be taken as a follow-up to this work which appear to be of some interest. Firstly, there are other systems than those covered here which could be handled by these techniques with comparable accuracy. Some excited states of the atomic systems covered here are one possibility. In particular, the lowest 2P , 2D , 2F series of states of lithium and its isoelectronic ions can be handled very easily, and probably with about the same accuracy as the ground state. It might also be of interest to look at the excited states of the same symmetry as the ground state. They are approximated to by the higher eigenvalues of the configuration interaction matrix. Molecular systems such as H_2^- , H_3 , He_2 , and LiH should also be obtainable to a similar accuracy as the isoelectronic atom.

Secondly, since the criterion of accuracy throughout this research has been the total energy, other properties computed with these wave functions should provide other interesting criteria of goodness for the configuration interaction type of approach—properties like hyperfine splitting, diamagnetic susceptibility, etc. In particular, one set of properties that bear looking at are transition probabilities. While they require excited states as well as the ground state, there is the nice feature that they can be computed by three different methods, the dipole length, velocity, and acceleration, all of which would be identical for the eigenfunction.

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¹⁷ R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).